



Separate measurement of current density under land and channel in Direct Methanol Fuel Cells



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HIGHLIGHTS

- Current densities under the land and channel are separately measured in DMFCs.
- Current density is much higher under the land than that under the channel.
- The main reason for the higher current density is the much higher ECA under the land.

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ABSTRACT

The knowledge of where current density is higher, under the land or channel in a direct methanol fuel cell (DMFC) and the mechanisms are very important for flow-field design optimizations. Such information could also lead to solutions to mitigate methanol crossover and/or its effects. Therefore, a novel technique is used to directly measure the current density under the land and under the channel separately. In this method, the anode side of the cell is partially catalyzed depending on the area of interest, whereas the cathode side is always fully catalyzed. Experimental results show that, under all the operating conditions used, the current density under the land is always significantly higher than that under the channel. Under most operating conditions, the current density under the land is more than 100% higher than that under the channel, and sometimes, as high as three times higher in typical DMFC operating voltage ranges. Further study shows that one of the main causes for such a drastic difference is the much higher electrochemical active area (ECA) under the land. Additional experimental results also show the performance trends for the land or the channel at different methanol concentrations and different cathode reactants (air or oxygen).

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1. Introduction

Direct methanol fuel cells (DMFCs) are an attractive option to power the next generation of digital cameras, mobile phones or even tablets, thanks to their compact design, quick refueling and low operating temperature. In their current status, DMFCs exhibit low power densities and as a result they are not yet the viable alternative to Lithium-ion batteries. This is because methanol crossover is a serious drawback to the cell performance and any advancement in DMFC technology is going to be hampered by such a phenomenon. Methanol crossover hinders the performance of the cell due to the formation of mixed potentials at the cathode. It also reduces the efficiency of the cell as it reduces fuel utilization. Methanol crossover and/or its effects can be mitigated via (a)

developing alternative membranes (e.g. Ref. [1]), (b) improving the electro-oxidation process in the catalyst layer and improving the structure of the catalyst and gas diffusion layers (e.g. Ref. [2]), and (c) optimizing the design of the flow field and the membrane electrode assembly (MEA) which can be achieved by studying the current density distributions (e.g. Ref. [3]).

The study of current density distribution in DMFCs is of a great importance for the optimization of cell designs and operations. Mench and Wang [4] reported that studying current distribution helps to understand the effects of water management, CO poisoning, and species distribution. Schroder et al. [5] stated that investigating the local distribution and transport behavior of CO₂ bubbles and water droplets at different operating conditions opens great possibilities for improving the fuel cell design. Ye et al. [6] suggested that optimizing the flow field geometry (land and channel widths as well as channel pattern) is essential to reach an even distribution of species and hence achieving a good cell

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performance. Ay et al. [7] gave many reasons for the importance of uniform current distribution; notably, it reduces the cost and increases the performance of the cell. Moreover, it ensures maximum lifetime for the cell components due to the decrease in corrosion processes in the cell. Saarinen et al. [8] reported that the complex relationships between different variables and operating conditions can be well understood through current distribution measurements. They also suggested that current distribution data can be useful in validating fuel cell models.

There are several experimental studies on current distribution measurement in DMFCs. Mench and Wang [4] measured the current distribution in a DMFC under steady state and transient conditions. Their measurement device allowed for the gas diffusion layer to be placed directly on electrically segmented lands. The results showed that current distribution in the cathode is nearly homogenous at high anode and cathode stoichiometries due to the fast removal of water in the cathode. However, current distribution in the cathode is far from being homogenous at low anode and cathode flow rates due to flooding. This shows that current mapping is effective in screening for low activity areas of the flow fields. It was concluded that water accumulation and pore-filling in the cathode GDL affect DMFC performance at low cathode stoichiometry. Ay et al. [7] analyzed the current distribution in DMFC at different operating conditions such as flow rate and methanol concentration by segmenting the current collector. They found that the difference between the current densities at the methanol inlet (maximum) and outlet (minimum) increases as the methanol concentration decreases from 1 M to 0.5 M. Furthermore, changing methanol flow rates affects the homogeneity of the current distribution; as methanol flow rate decreases, the current density distribution becomes less homogenous. When oxygen was used instead of air, the group observed more current density fluctuation from inlet to outlet. Park et al. [9] used a commercial current-mapping device called Current Scan Lin to study current distribution in a single and a five-line serpentine flow fields under various

operating parameters. They indicated that current density distribution is inhomogeneous when the cell temperature or the oxidant flow rate in the cathode is lower. At low temperatures, water cannot easily be vaporized causing flooding near the cathode outlet. Unevenness in current distribution can also be caused by low cathode flow rate, higher load current and higher methanol concentration. When low current was imposed on the cell, methanol flow rate did not affect the homogeneity of the current distribution. However, at higher current, methanol flow rate did affect the homogeneity of the current distribution. This is due to the evolution of CO_2 gas and partial drying of the membrane near the cathode inlet. Moreover, they concluded that flow field configuration affects the homogeneity of the current distribution. Schroder et al. [5] studied current and fluid distribution in DMFC by using high resolution neutron radiology coupled with a segmented fuel cell. Neutron radiology was used due its high attenuation coefficient for hydrogen rich species compared to the solid components of the fuel cell. Therefore, this technique allows for water droplets and CO_2 bubbles to be observed. The anode side of the cell was operated under normal DMFC conditions, but two different air flow rates were supplied to the cathode side; one is high and the other is low for a cell size of $4.2 \times 4.2 \text{ cm}^2$. The group concluded that flooding in the cathode is responsible for up to 30% loss in performance due to inhomogeneous current distribution. Furthermore, they confirmed the existence of a bi-functional operation in the cathode and measured the current distribution in the region. Saarinen et al. [8] investigated mass transport including methanol crossover in a free-breathing direct methanol fuel cell. They measured current distribution along the anode flow channels and used this information to determine local reactants concentration. This was accomplished by segmenting the cathode flow field into 48 segments. They observed that current density distribution becomes less even as methanol concentration increases (due to methanol crossover) and cell temperature decreases (due to an increase in air convection and a decrease in activation overpotential at the electrodes). It was

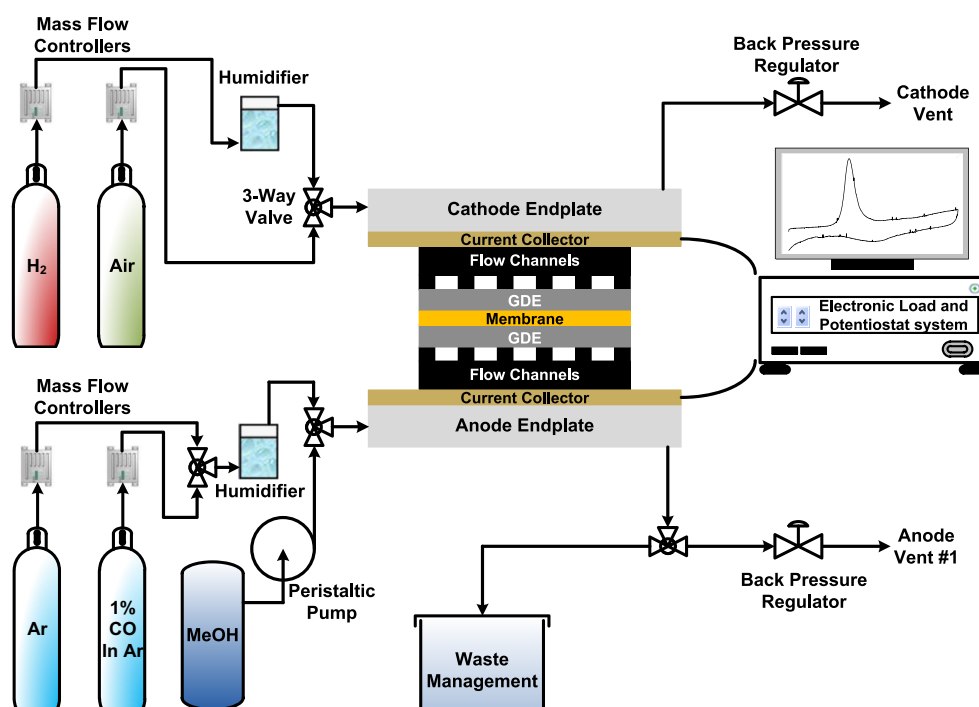


Fig. 1. Schematic of the experimental system.

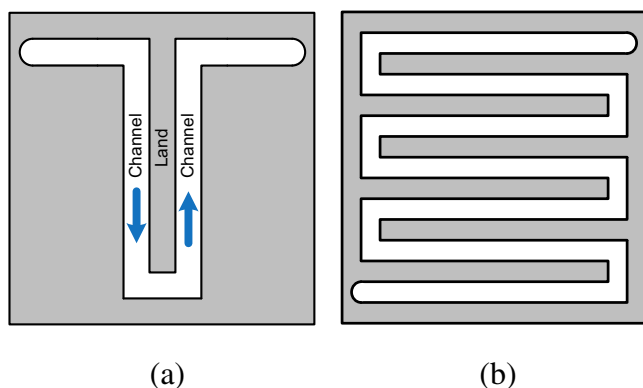


Fig. 2. Schematic (not to scale) of the bipolar plates used; (a) anode (b) cathode.

concluded that power production in a free-breathing DMFC depends on the local oxygen concentration and affected by insufficient air convection and high methanol crossover.

As can be seen from above, all of the experimental studies devoted to study current distribution in DMFC were focused on measuring the local current from segments that cover multiple channels and lands of the flow field plate. Moreover, no experimental work has been done to separately measure current under the land and channel in DMFCs. It is believed that the separate measurement of current density under the land and the channel in DMFCs can lead to practical solutions to mitigate the effects of methanol crossover. Therefore, the objective of this work is to separately measure the current density under the land and under the channel to determine where the current density is higher and provide mechanistic explanations.

2. Experimental system and methodology

2.1. Fuel cell testing system

The fuel cell testing system used in this work is a fuel cell test station manufactured by Hydrogenics Corp. (Vancouver, Canada). The test station controls the flow rate, temperature, pressure and humidity of the flowing gases as well as the cell temperature. The testing system is coupled with a potentiostat (VersaStat 3, Princeton Applied Research, Inc.) capable of data averaging during acquisition to serve as a load bank that controls the load on the fuel cell and measures the potential and current of the cell. Moreover, VersaStat 3 is used to conduct CO stripping voltammetry measurements. Methanol is pumped to the anode side of the fuel cell using a Gilson Minipuls 3 pump. Fig. 1 shows the schematic of the experimental system.

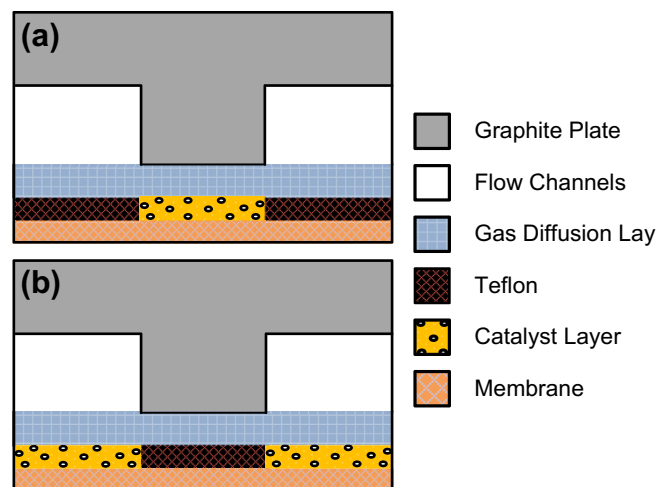


Fig. 4. Cross-section of the anode side; (a) land area is catalyzed (b) channel areas are catalyzed.

2.2. Fuel cell fixture and membrane electrode assembly (MEA)

The fuel cell fixture used in this study was designed in-house. The cathode and the anode graphite plates were machined with single serpentine flow field. However, the anode was machined with a single pass serpentine while the cathode was machined with multiple passes of the same flow field design; Fig. 2 shows a schematic of the bipolar plates used. The cell was assembled in such a way that the flows in the anode and cathode sides were in cross-flow; i.e. the channels were perpendicular.

Three custom-made MEAs were purchased from Fuel Cells Etc (College Station, Texas). The membrane used in the MEAs was Nafion® 117 and the gas diffusion electrodes were made of carbon cloth with a catalyst loading of 4 mg cm^{-2} PtRu (atomic ratio of 1:1) in the anode and 2 mg cm^{-2} Pt/Black in the cathode. The special design is based on the works of Wang and Liu [10] as well as Higier and Liu [11]; the cathode side has a constant area of 50 cm^2 , while the anode was partially catalyzed and therefore its active area varies depending on the catalyzed part as shown in Figs. 3 and 4. Teflon was used to insulate the partially catalyzed areas from other areas (catalyzed or non-catalyzed regions).

The break-in procedure for all MEAs was identical. First, to activate the MEA, humidified nitrogen gas at 80°C and 1000 sccm (sccm = standard cubic cm per min) was fed to both sides of the fuel cell for 6 h. Second, to activate the catalyst layer, humidified hydrogen at 70°C and 500 sccm was fed to the anode while humidified oxygen at 70°C and 1500 sccm was fed to the cathode. Then the fuel cell was run under constant voltage of 0.6 V and the

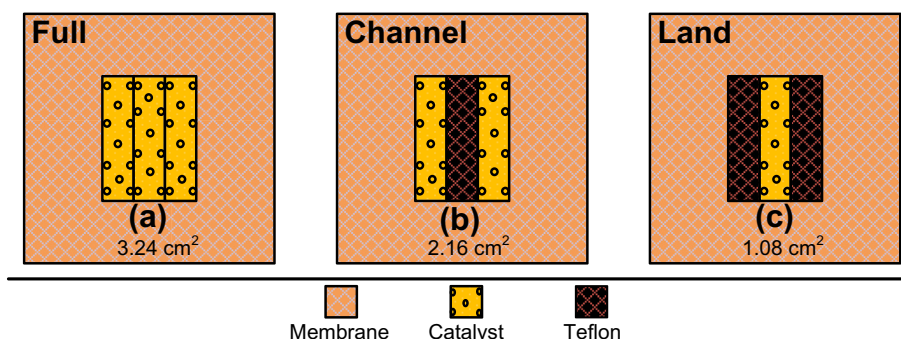


Fig. 3. Schematic of the anode active area; (a) anode is fully catalyzed (b) channel areas are catalyzed (c) land area is catalyzed.

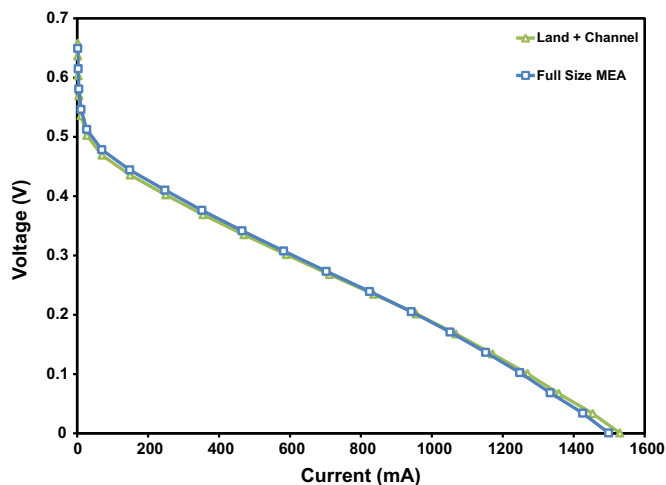


Fig. 5. Validation of the technique of separate current measurement under the land and channel in a DMFC. Conditions: methanol concentration 2 M and flow rate 1 ml min⁻¹.

current response was monitored. After a steady state current was reached, the break-in process was considered to be completed.

2.3. Validation of the experimental methodology

The experimental methodology has been validated for H₂/O₂ PEM fuel cells for both parallel [10] and serpentine [12] flow fields. One would think that the results may be similar to those of PEMFC;

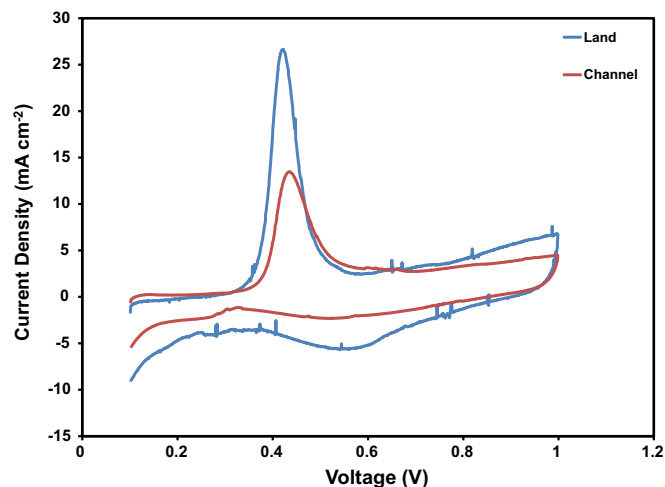


Fig. 7. CO stripping voltammograms for land and channel areas.

however, due to the significant differences between the two types of fuel cells (two phase flow in the anode and methanol crossover from the anode to the cathode), it is necessary to validate the experimental methodology to be used in DMFCs.

A series of experiments were conducted in order to validate the experimental methodology and the results for the case for 2 M methanol concentration flowing at 1 ml min⁻¹ and a cell temperature of 70 °C are shown in Fig. 5. It is clear that the sum of the currents produced by the MEA with catalyzed land area and the currents produced by the MEA with catalyzed channel areas equal

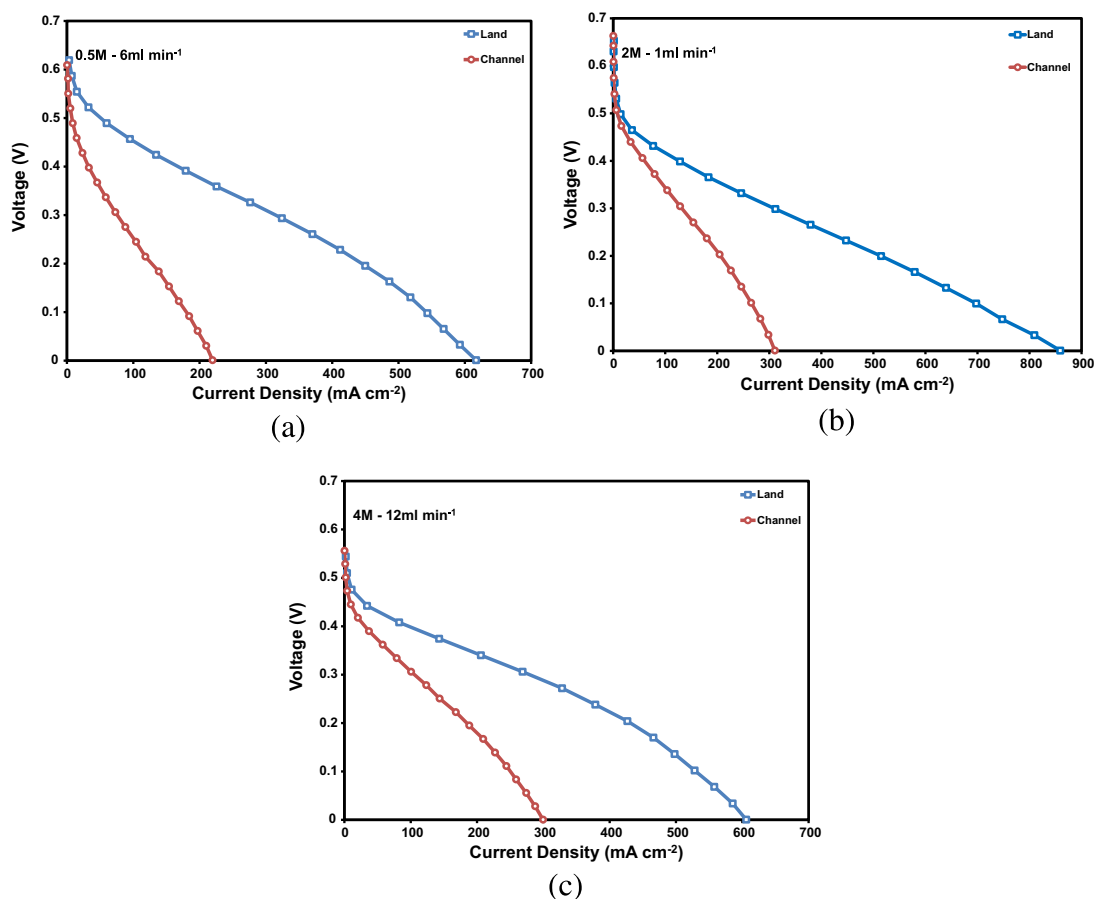


Fig. 6. Comparison between land and channel performances for (a) 0.5 M flowing at 6 ml min⁻¹, (b) 2 M flowing at 1 ml min⁻¹ and (c) 4 M flowing at 12 ml min⁻¹.

Table 1
ECA values for land and channel.

	ECA ($\text{cm}^2_{\text{Pt}} \text{mg}^{-1}_{\text{Pt}}$)	Percent increase
Land	270.1	48.5%
Channel	181.8	

to that produced by the full MEA. In other words, case (b) + case (c) = case (a) in Fig. 3. Therefore, these results demonstrate that the technique of individually measuring the current under the land and under the channel can indeed be extended to DMFCs.

2.4. Electrochemical measurements

Polarization curves are the simplest way for fuel cell evaluations. These performance curves were obtained by running methanol in the anode and humidified air or oxygen in the cathode at a flow rate of 2000 sccm. The fuel cell temperature was set at 70 °C and the operating pressure was atmospheric pressure. Each curve was obtained by averaging three polarization curves acquired at identical operating conditions. The individual polarization curves were obtained by scanning the voltage from 0 V vs. OCV to 1 mV vs. REF. at a scan rate of 10 mV s⁻¹.

CO stripping voltammetry is a technique used to determine the electrochemical active area (ECA) of PtRu electrode in DMFC anodes through the oxidation of adsorbed CO. The ECA ($\text{cm}^2_{\text{Pt}} \text{mg}^{-1}_{\text{Pt}}$) of a PtRu electrode is defined by [13]:

$$\text{ECA}(\text{anode}) = \frac{\text{Charge}(\mu\text{C cm}^{-2})}{484(\mu\text{C cm}^{-2}) \times \text{Catalyst loading}(\text{mg Pt cm}^{-2})} \quad (1)$$

Gasteiger et al. [14] was the first to use this method to study bulk PtRu alloys with a range of surface compositions. Liu et al. [15] reported that the coverage of CO on Ru is significantly lower than on Pt; therefore, the ECA found using this method represents the true value of the area available for the electrochemical reaction. CO stripping voltammograms were acquired *in situ* according to the method proposed by Dinh et al. [16]. In the current study, the anode side was supplied with humidified Ar or CO plus Ar and serving as a working electrode. Meanwhile, the cathode side was supplied with humidified hydrogen and hence acting as pseudo-reference dynamic hydrogen electrode (DHE). The cell temperature was set at 35 °C. When 1% CO in Ar is flowing in the anode, CO will adsorb onto the PtRu electrode. This process lasted for 30 min and the voltage was held at a constant voltage of 0.1 V against DHE. Then the gas was switched to Ar to remove any CO from the gas phase while still keeping the voltage constant at 0.1 V. After sufficient time has lapsed (30–60 min), the CO stripping voltammograms were recorded by scanning the potential from 0.1 V to 1 V at a scan rate of 5 mV s⁻¹.

3. Results and discussion

3.1. Performance comparison between land and channel

Several sets of experiments were conducted to directly compare the performances of the land and channel areas; three of these sets are shown in Fig. 6. It can be seen that the land significantly outperformed the channel under all the operating conditions used. Under most operating conditions, the current density under the land is more than 100% higher than that under the channel, and

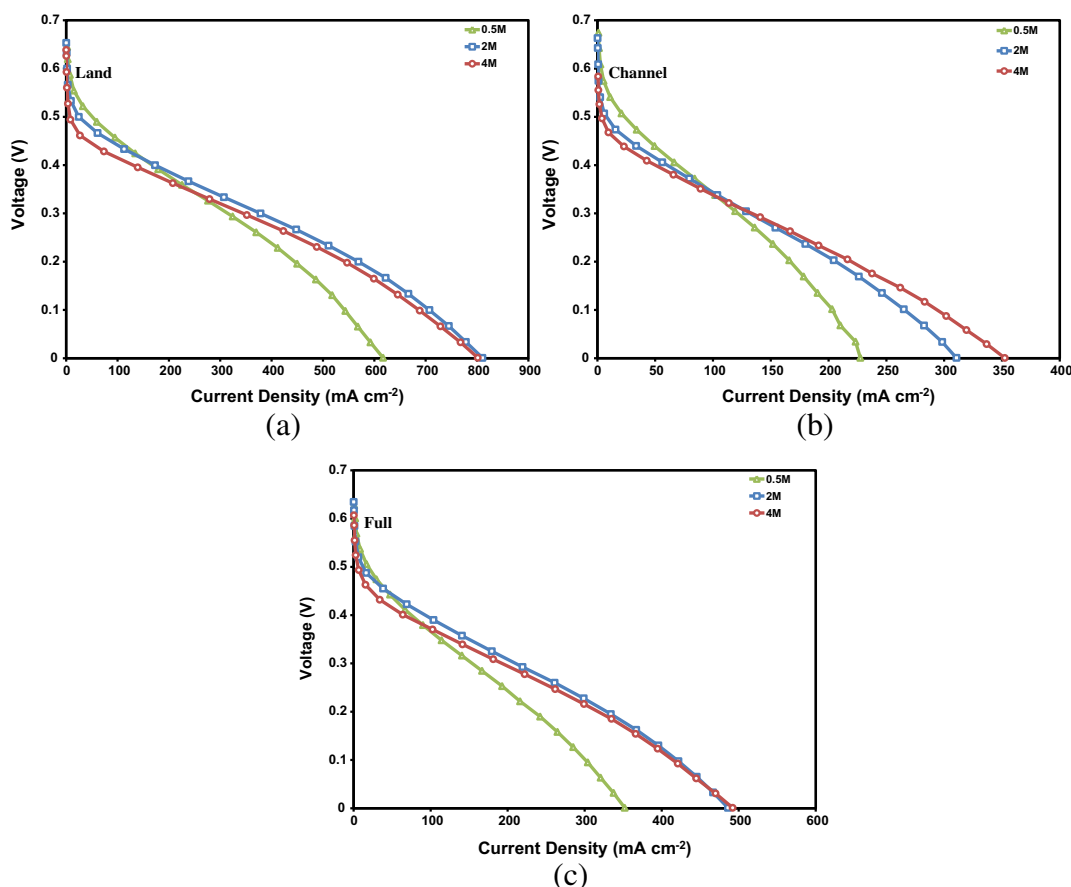


Fig. 8. Polarization curves at different methanol concentrations for (a) land (6 ml min⁻¹), (b) channel (1 ml min⁻¹) and (c) full MEA (6 ml min⁻¹).

sometimes, as high as three times higher in typical DMFC operating voltage ranges.

Since concentration losses are negligible in the low and intermediate current density regions, another factor must be the cause for the higher land performance. By examining Meyers and Newman [17] derivation for the kinetics of methanol oxidation at the anode and the cathode, one can conclude that the performance of the cell is greatly affected by the specific surface area (a). The specific surface area is defined by Marr and Li [18] as:

$$a = \frac{m_{\text{pt}} \text{ECA}}{\delta^{\text{cl}}} \quad (2)$$

where m_{pt} is the catalyst loading and δ^{cl} is the catalyst layer thickness. Since both the land and the channel have identical catalyst loading and thickness, then the specific surface area is only affected by the ECA. The ECA values were calculated using Eq. (1) for both the land and the channel via CO stripping voltammetry. The results of the measurements are displayed in Fig. 7. It is evident from the voltammograms that the land has a much higher peak compared to that of the channel; indicating that it has a larger ECA value. In fact, as presented in Table 1, the ECA under the land is approximately 48.5% higher than that under the channel.

Similar results were reported for H_2/O_2 PEM fuel cells [10,11]; however, in DMFCs, the land performance is higher than that of the channel in the entire current density region. In other words, unlike H_2/O_2 PEM fuel cells, DMFCs do not exhibit the crossing point phenomenon in which the current densities under the land and the channel are equal. This is strange because one would think that under the land the methanol concentration would be lower due to the higher mass transfer resistance. These results indirectly show that the concentration of methanol in the catalyst layer under the land is higher than that under the channel. Since the bipolar plate used in these experiments has a serpentine flow pattern, then the mode of mass transport in the GDL and the catalyst layer under the channel is diffusion while it is a combination of diffusion and convection under the land. Thus it is highly possible that the effect of under land convection in DMFC is significant and causes a higher methanol concentration in the catalyst layer under the land. Under land convection in DMFCs is going to be studied in a future work.

3.2. Land and channel individual performances

In this section, the effects of operating conditions such as methanol concentration and the type of cathode reactant on the individual performances of the land and the channel are studied.

3.2.1. Different methanol concentrations

The polarization curves for the MEA with catalyzed land only and the MEA with catalyzed channels only at different methanol concentrations are displayed in Fig. 8 (a) and (b), respectively. The results show that the performances of the land and channel in the activation region have a similar pattern. It can be seen that in the low current density region, the cell performance decreases with the increase in methanol concentration from 0.5 M to 4 M. This is mainly due to the increase in mixed potential as a result of the increase in methanol crossover rate.

In the high current density region, both the land and channel, the polarization curves with 0.5 M methanol concentration are the lowest because of the concentration effect, which is evident due to the sharp drop in performance. From Fig. 8 (a) and (b), one can notice that the current densities under both the land and the channel increase with methanol concentration; indicating the availability of reactants as current increases. Besides, as current density increases, the methanol crossover rate decreases, thus the

effect of mixed potential decreases, leading to higher cell performance for higher methanol concentrations.

The performance of the full MEA is a weighted average of the land and channel and results are shown in Fig. 8 (c). A similar pattern is also reported in the literature for DMFCs (e.g. Refs. [19–21]). This could only suggest that the overall cell performance of a DMFC at a constant flow rate and varying methanol concentration is significantly influenced by the performance of the land, since the land significantly outperforms the channel. For the full MEA, the highest power density is achieved with 2 M methanol concentration, consistent with the widely reported optimum methanol concentration of 1–2 M, due to the balance between the negative effect of methanol crossover and the positive effect of higher concentration.

3.2.2. Different cathode reactants

In order to determine the effects of the type of the cathode reactant on the performance under land and channel, two sets of experiments were conducted using either oxygen or air as the cathode reactant. The results are presented in Fig. 9 (a) and (b). Comparing these two figures, it is clear that when oxygen is used in the cathode, similar trend exists, i.e. the current density under the

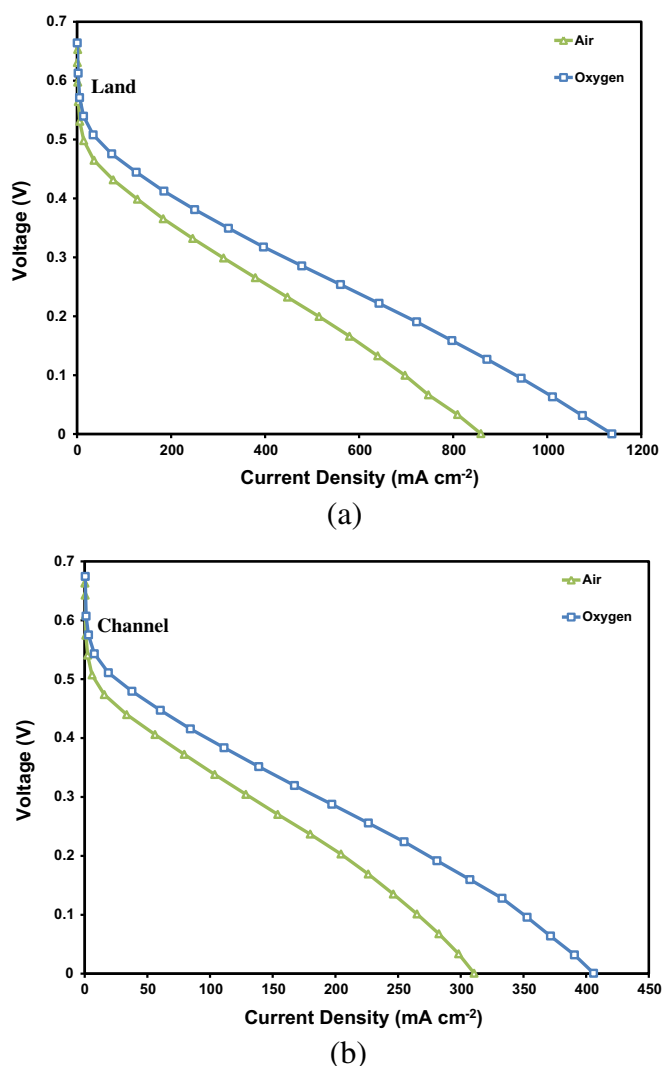


Fig. 9. Polarization curves for different cathode reactants for (a) land, and (b) channel. Conditions: methanol concentration 2 M and flow rate 1 ml min⁻¹.

land is significantly higher than that under the channel. For both air and oxygen, the current density under the land is more than double that under the channel at the same operating conditions. It is also evident that the performances of the land and channel with oxygen are much higher than those for air. The reason, according to Ge and Liu [21], is that when enough oxygen supply to the cathode side, the adverse effect of methanol crossover is reduced. It is believed that when the permeated methanol to the cathode can be oxidized faster, more reaction sites will be free for oxygen reduction reaction (ORR).

4. Conclusion

A novel technique was used to directly measure the current density under the land and channel in a DMFC. In this method, the anode side of the cell was partially catalyzed depending on the area of interest (land, channel or full) whereas in the cathode side the full MEA is always catalyzed. From the experimental results, the following conclusions can be made:

- Under all the conditions used, current density under the land is always significantly higher than that under the channel.
- The main cause for the much higher current density under the land is the significantly higher ECA under the land area.
- For both land and channel areas, a similar pattern exists for different methanol concentrations in different cell voltage regions.
- The optimal methanol concentration for the land area and the full cell is around 2 M, in agreement with the widely reported optimum methanol concentration of 1–2 M.
- When oxygen is used, current density under the land is also significantly higher than that under the channel.

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References

- [1] Yongsheng Wei, Saif Matar, Liangbo Shen, Xinwei Zhang, Zhijun Guo, Hong Zhu, Hongtan Liu, *International Journal of Hydrogen Energy* 37 (2) (January 2012) 1857–1864.
- [2] Saif Matar, Hongtan Liu, *Electrochimica Acta* 56(1) (15 December 2010) 600–606.
- [3] Andrew Higier, Hongtan Liu, *International Journal of Hydrogen Energy* 35 (5) (March 2010) 2144–2150.
- [4] M. Mench Matthew, C.Y. Wang, *Journal of Electrochemical Society* 150 (2003) A79.
- [5] A. Schroder, Klaus Wippermann, Jurgen Mergel, Werner Lehnert, Detlef Stolten, Tilman Sanders, Thorsten Baumhofer, Dirk U. Sauer, Ingo Manke, Nikolay Kardjilov, Andre Hilger, Jana Schloesser, John Banhart, Christoph Hartnig, *Electrochemistry Communications* 11 (8) (2009) 1606–1609.
- [6] Q. Ye, T.S. Zhao, C. Xu, *Electrochimica Acta* 51 (25) (2006) 5420–5429.
- [7] F. Ay, A. Ata, H. Dohle, T. Sener, H. Gorgun, *Journal of Power Sources* 167 (2) (2007) 391–397.
- [8] V. Saarinen, O. Himanen, T. Kallio, G. Sundholm, K. Kontturi, *Journal of Power Sources* 163 (2) (2007) 768–776.
- [9] S.M. Park, Sang-Kyung Kim, Seongyop Lim, Doo-Hwan Jung, Dong-Hyun Peck, Won Hi Hong, *Journal of Power Sources* 194 (2) (2009) 818–823.
- [10] Lin Wang, Hongtan Liu, *Journal of Power Sources* 180 (1) (15 May 2008) 365–372.
- [11] Andrew Higier, Hongtan Liu, *Journal of Power Sources* 193 (2) (5 September 2009) 639–648.
- [12] Andrew Higier, *An In-situ and Ex-situ Investigation of Current Density Variations in a Proton Exchange Membrane Fuel Cell*. Ph.D. dissertation, University of Miami, 2010.
- [13] A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini, L. Giorgi, *Journal of Power Sources* 105 (1) (2002) 13–19.
- [14] H.A. Gasteiger, N. Markovic, P.N. Ross Jr., E.J. Cairns, *The Journal of Physical Chemistry* 98 (2) (1994) 617–625.
- [15] R. Liu, H. Iddir, Q. Fan, G. Hou, A. Bo, K.L. Ley, E.S. Smotkin, Y.E. Sung, H. Kim, S. Thomas, A. Wieckowski, *The Journal of Physical Chemistry B* 104 (15) (2000) 3518–3531.
- [16] H.N. Dinh, X. Ren, F.H. Garzon, P. Zelenay, S. Gottesfeld, *Journal of Electroanalytical Chemistry* 491 (1–2) (2000) 222–233.
- [17] J.P. Meyers, J. Newman, *Journal of the Electrochemical Society* 149 (2002) A718–A728.
- [18] Curtis Marr, Xianguo Li, *Journal of Power Sources* 77 (1) (1 January 1999) 17–27.
- [19] M.K. Ravikumar, A.K. Shukla, *Journal of the Electrochemical Society* 143 (8) (1996) 2601–2606.
- [20] Doo Hwan Jung, Chang Hyeong Lee, Chang Soo Kim, Dong Ryul Shin, *Journal of Power Sources* 71 (1–2) (15 March 1998) 169–173.
- [21] J. Ge, H. Liu, *Journal of Power Sources* 142 (1–2) (2005) 56–69.